

# RAW MATERIALS

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## USE OF WOLLASTONITE IN NONFRITTED ZIRCONIUM GLAZES

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The possibility of using wollastonite as one of the main components in non-fritted opacified glazes for sanitary ceramics is demonstrated. The main physicochemical properties of synthesized coatings are determined, the specifics of their structure and phase composition are analyzed.

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A topical problem of ceramic production is the expansion of material resources for the porcelain-faience industry and simultaneous upgrade of product quality. Wollastonite is of great interest in this respect.

This raw material is white-colored powder belonging to pyroxenoides made up by  $[\text{SiO}_4]$  tetrahedron chains, whose bases are not in the same plane, even approximately, but are differently oriented in such a way that the chain pattern is repeated after each third tetrahedron. Two modifications of wollastonite are known:  $\alpha$ - $\text{CaSiO}_3$  (pseudowollastonite) and  $\beta$ - $\text{CaSiO}_3$  (proper wollastonite), which are closely interrelated [1]. Pseudowollastonite crystallizes in the pseudo-hexagonal syngony and wollastonite in the triclinic syngony. At a temperature of 1125°C wollastonite is irreversibly transformed into pseudowollastonite with a slight volume alteration. Its melting temperature is 1540°C, the density of  $\alpha$ -wollastonite is  $3.09 \times 10^3 \text{ kg/m}^3$ , and that of  $\beta$ -wollastonite  $2.87 \times 10^3 \text{ kg/m}^3$ . Its Mohs hardness is 4.5–6.0. The CLTE of  $\alpha$ -wollastonite is  $118 \times 10^{-7} \text{ K}^{-1}$ , and that of  $\beta$ -wollastonite  $65 \times 10^{-7} \text{ K}^{-1}$ . Wollastonite crystals have a needle-like shape; besides, fibrous and discoid crystals are found as well [2].

Analysis of published data [2, 3] indicates that wollastonite is most frequently used in the production of construction materials, in particular, in the production of facing tiles. Wollastonite additives range from 15 to 65% (here and elsewhere wt.%) depending on the chemical composition. It is known that wollastonite is used in the production of low-melting glazes, which makes it possible to lower the frit content to 20% and, accordingly, decrease the cost of the glaze. However, no published data have been found on the use of this component in nonfritted glazes and its effect on the properties of coatings.

We have attempted to fill this vacancy in the systematic study of the physicochemical (luster, whiteness, CLTE, microhardness) properties of coatings and to reveal a correlation between the said properties and the compositions of nonfritted glazes for sanitary ware made from porcelain mixtures.

For our study we selected wollastonite concentrate VP-25 (hereafter “wollastonite”) produced by the Trans-Resurs Company (Russia) according to standard TU 5726-001-50889697-01. The averaged chemical composition of wollastonite is as follows (%): 50.00  $\text{SiO}_2$ , 0.16  $\text{Fe}_2\text{O}_3$ , 45.20  $\text{CaO}$ , and 0.61 calcination loss.

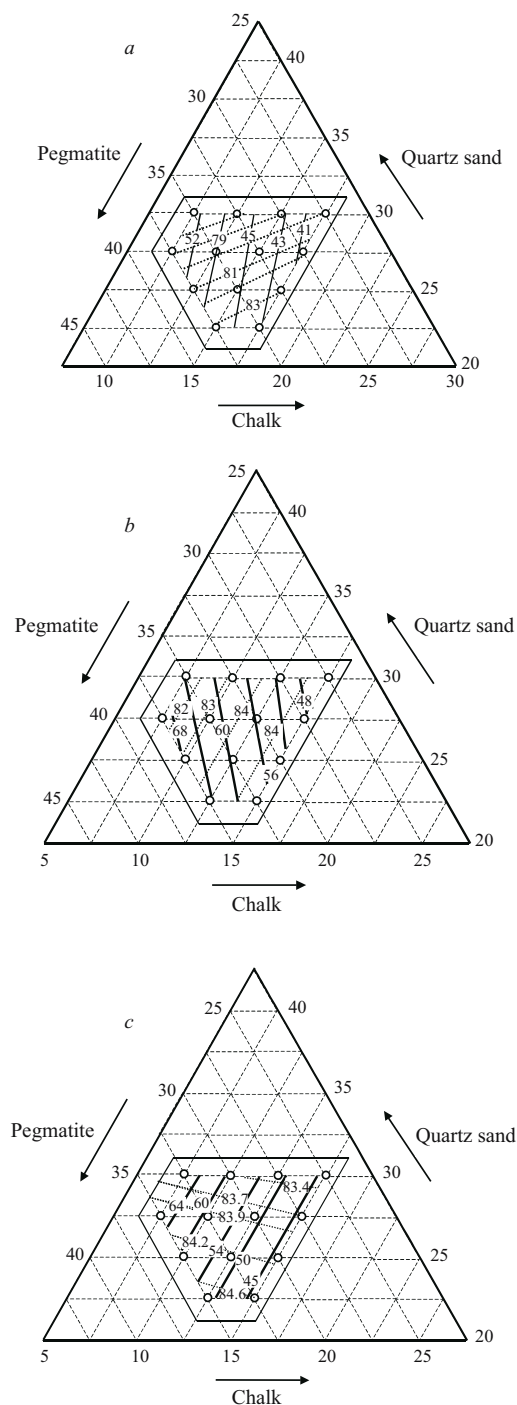
X-ray phase analysis of wollastonite concentrate indicated that the material mainly includes wollastonite;  $\alpha$ -quartz is present in insignificant quantities.

Wollastonite concentrate was introduced in an amount of 55% into previously analyzed glazes of series 1, 2, and 3 [3] with zircosil content equal to 10.0, 12.5, and 15.0%, respectively; the sections were numbered 5, 6, and 7, respectively. The following natural materials were used: Belgorodskoe chalk, Chupinskoe pegmatite, Novoselkovskoe quartz sand, zircosil, refractory clay Granitik-Vesko, and Glukhovetskoe kaolin.

Glaze slips were prepared using the traditional ceramic technology. Suspensions were deposited on molded sanitary ware that had been dried to residual moisture not more than 1% and fired for 22 h with an 1.5 h exposure at the maximum temperature (1180–1200°C) in a Sacmi tunnel furnace under the industrial conditions at the Keramin Company. The CLTE of the ceramic base was  $57.7 \times 10^{-7} \text{ K}^{-1}$ .

Visual inspection of fired samples showed that the opacity of coating increases as the content of  $\text{ZrO}_2$  in the batch grows from 6.5% (equivalent to 10% zircosil) to 7.88% (15% zircosil). The opacity of coatings was determined by the most common method: measuring their whiteness.

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**Fig. 1.** Luster and whiteness isolines for the fifth (a), sixth (b) and seventh (c) sections of the considered system: a) 10.0 % zircosil, 5.5% wollastonite, 5.5% refractory clay, and 4.5% kaolin; b) 12.5% zircosil, 5.5% wollastonite, 5.5% refractory clay, and 4.5% kaolin; c) 15% zircosil, 5.5% wollastonite, 5.5% refractory clay, and 4.5% kaolin; ..... whiteness (%); —) luster (%); ○) considered compositions; —) boundaries of the considered composition range.

The luster and whiteness of experimental samples were determined on a BF-2 photoelectric luster meter.

The effect of the composition on the luster and whiteness of coatings in the considered systems for the purpose of de-

termining the optimum composition range was studied using the Statistika data-processing package. The obtained results are shown in Fig. 1 in the form of isolines. The variation of whiteness in all considered series is similar: it grows with increasing chalk content due to the proportional decrease in the amount of pegmatite and quartz sand. The luster of coatings varies in the opposite direction.

Comparative analysis of three series of coatings suggests that the optimum section in the considered system of components is the one with 12.5% zircosil, which yields relatively high luster (48 – 68%) and whiteness (82 – 85%) values compared to 41 – 52 and 78 – 83%, respectively, in the section with 10% zircosil and 45 – 64 and 82 – 85% in the section with 15% zircosil.

A prerequisite for high-quality coatings for sanitary ceramic ware is a high degree of whiteness and luster, which requires uniform crystallization. Moreover, crystal sizes should not exceed a certain level to prevent the formation of dull surfaces.

The viscosity of an emerging glaze melt has a critical effect on the crystallization process. Analyzing each section, it can be stated that for an equal content of the opacifier (zircosil), the viscosity decreases with increasing content of chalk (CaO), which is responsible for an increased quantity of non-bridge oxygen atoms and Ca–O bonds, whose strength is several times weaker than the strength of Si–O bonds. Note that CaO to a greater extent decreases viscosity in the high-temperature range and to a lesser extent in the low-temperature range. The mobility of the particles in the high-temperature range is high and the emerging crystallization centers are unstable. As temperature decreases (the cooling process), the stability of the centers grows and the rate of nuclei formation grows significantly. As a result, crystal phases are intensely formed in cooling, mainly zircon which is responsible for the opacification of glaze. Furthermore, note that a decrease in the glaze melt viscosity within the crystallization temperature interval may produce volumetric crystallization, as well as surface crystallization, which ought to increase the degree of opacity of the coatings. Analysis of luster and whiteness of the coatings in the sections with different quantities of zircosil indicates that the opacity of coatings increases as the content of the latter grows from 10 to 15%. With 15% zircosil content not only the quantity of the crystalline phase grows, but the crystal sizes grow as well, which leads to the formation of semidull coatings in this section, along with lustrous one. The zirconium ion, due to its relatively high charge (+4) and a small radius (0.082 nm), loosens the Si–O–Si bonds.

X-ray phase analysis corroborates the crystallization structure of the samples. It is established that introducing wollastonite concentrate together with the formation of zircon  $\text{ZrSiO}_4$  and  $\alpha$ -quartz leads to the crystallization of a new phase, namely  $\text{Ca}_2\text{ZrSi}_4\text{O}_{12}$ , whose presence had not been identified in any of the preceding series (i.e., in the absence of wollastonite concentrate in the batch composition); be-

sides, small quantities of proper wollastonite  $\text{CaO} \cdot \text{SiO}_2$  are registered. Increasing the zircosil content to 15% leads to the disappearance of the diffraction maxima of the last two phases (Fig. 2) and a certain increase in the intensity of the zircon peaks. This is caused by the growing melt viscosity and the saturation of the melt by zirconium ions, which facilitates the crystallization of  $\text{ZrSiO}_4$ .

Based on the phase diagram of the three-component system  $\text{CaO} - \text{ZrO}_2 - \text{SiO}_2$ , the phase  $\text{Ca}_2\text{ZrSi}_4\text{O}_{12}$  is expected to be formed at a temperature of  $1400^\circ\text{C}$ . Crystals of this particular phase presumably belong to the rhombic syngony with light refraction indexes  $n_g = 1.658$  and  $n_p = 1.653$ , density  $3060 \text{ kg/m}^3$ , and  $\text{CLTE } 59 \times 10^{-7} \text{ K}^{-1}$  [4]. The formation of this compound at the firing temperature ( $1180 - 1200^\circ\text{C}$ ) is due to the multicomponent state of the melt, which leads to the formation of eutectics and a crystal phase at temperatures that are below the theoretical values.

As the degree of opacification and the surface textures depend not only on the quantity of the opacifier, but on the size of the opacifying particles as well, we investigated the surface structure using electron microscopy. The obtained data indicate that a zircosil content equal to 10.0, 12.5, and 15.0% corresponds to the formation of about 30, 40, and 45% crystalline phase. The comparison of crystal sizes and their distributions indicated that glaze series 5 and 7 have more coarse crystals (20 and 30% of the total quantity, respectively) than series 6 (10%). Series 5 and 6 also contain needle-shaped wollastonite crystals up to 18 and  $10 \mu\text{m}$  long, respectively. The size of the fine isometric zircon crystals does not exceed  $1 \mu\text{m}$  in all series. The crystals of  $\alpha$ -quartz have an irregular shape and size ranging from 4 to  $17 \mu\text{m}$ . It was impossible to identify  $\text{Ca}_2\text{ZrSi}_4\text{O}_{12}$  crystals, which had been revealed in x-ray phase analysis, on the electron microscope photos.

Thus, the introduction of 10% zircosil into the batch is not sufficient for a subsequent crystallization of the opacifying phase at the specified melt viscosity. Increasing the opacifier content to 15% produces intense crystallization with a simultaneous increase in the crystal size, which contributes to the formation of a semidull surface. The introduction of 12.5% zircosil ensures good esthetic properties to products, which is presumably due to an optimal ratio of the crystal sizes and quantity.

The formation of a high-viscosity vitreous phase saturated with zirconium and silicon ions decreases the CLTE to  $(53 - 58) \times 10^{-7} \text{ K}^{-1}$  compared with the mixtures containing 10.0 and 12.5% zircosil:  $(57 - 65) \times 10^{-7}$  and  $(55 - 64) \times 10^{-7} \text{ K}^{-1}$ , respectively.

The microhardness of the glazes in all three sections is within the limits of 6100 – 7000 MPa and regularly grows as the content of chalk and pegmatite decreases, while the content of quartz sand increases.

Considering the obvious improvement in the external appearance of coatings on introducing wollastonite concentrate, further investigations were directed to studying its ef-

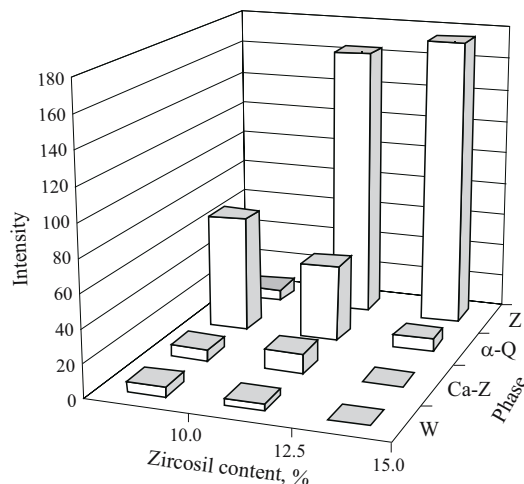


Fig. 2. Dependence of the relative intensity of diffraction maxima of the crystalline phases on the content of zircosil in the glaze: W) wollastonite; Ca-Z)  $\text{Ca}_2\text{ZrSi}_4\text{O}_{12}$ ;  $\alpha$ -Q)  $\alpha$ -quartz; Z) zircon.

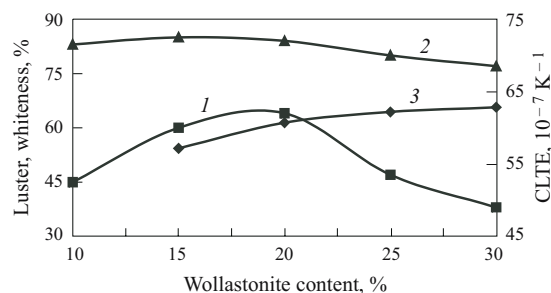


Fig. 3. Dependence of physicochemical properties on the composition: 1) luster; 2) whiteness; 3) CLTE.

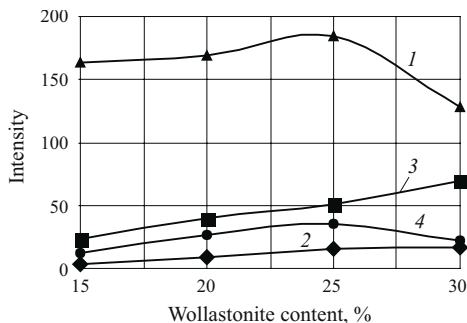
fect on the properties of glazes. The quantity of the concentrate introduced varied from 5 to 30% with an interval of 5% and a proportionate decrease in the content of pegmatite and quartz sand.

Since calcium oxide is introduced via wollastonite concentrate, it was decided to exclude chalk from the batch, which was expected to improve the quality of surfaces due to the decreasing gas emission under thermal treatment and, accordingly, would increase the luster of the coatings.

The visual evaluation of the samples indicated that upon introducing 5 to 10% wollastonite, we registered underfiring and only a slight fusion of the coating; from 15 to 20% we saw the formation of defect-free lustrous and semidull coatings; from 25 to 30% dull coatings were formed.

The study of the physicochemical properties of the samples (Fig. 3) shows that the content of wollastonite concentrate which provides good luster and whiteness and the required CLTE is equal to 15%.

The phase composition of these samples also includes zircon,  $\alpha$ -quartz, wollastonite, and  $\text{Ca}_2\text{ZrSi}_4\text{O}_{12}$ . The dependence of the intensity of diffraction maxima on the composition is represented in Fig. 4. As the content of wolla-



**Fig. 4.** Dependence of the relative intensity of diffraction maxima of crystalline phase on the composition: 1) zircon; 2)  $\text{Ca}_2\text{ZrSi}_4\text{O}_{12}$ ; 3)  $\alpha$ -quartz; 4) wollastonite.

stonite concentrate grows to 25%, the intensity of the diffraction maxima of all crystal phases grows and is accompanied by the regular transition of surface textures from semidull to lustrous; at 25% wollastonite content, semidull surfaces are formed again. Then the intensity of the zircon peaks decreases, which is related to the formation of a low-viscosity melt impeding the formation of crystallization centers and a further growth of the opacifying phase crystals, which is corroborated by the data of the whiteness of the coatings (Fig. 3).

With respect to thermal and chemical resistance, the samples were found to satisfy the requirements imposed by GOST 13449–82.

The studies performed confirm the advisability of using wollastonite concentrate as one of the main components in nonfritted opacified glazes for sanitary ceramics. It is established that the presence of 15% wollastonite concentrate in the considered system of components is necessary and sufficient. The optimum compositions have good spreading and relatively high luster and whiteness parameters. The CLTE of the optimum composition is  $53 \times 10^{-7} \text{ K}^{-1}$ , which is slightly lower than the CLTE of the ceramic base and, accordingly, ensures the required heat resistance of the product. All this confirms the advisability of using wollastonite concentrate in nonfritted glazes under high-temperature firing.

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